

Tweaking the Optoelectronic Properties of S-Doped Polycyclic Aromatic Hydrocarbons by Chemical Oxidation

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Dedicated to Prof. Alain Krief on the occasion of his 80th birthday.

Abstract: *Peri*-thiaxanthenothioxanthene, an S-doped analog of *peri*-xanthenoxanthene, is used as a polycyclic aromatic hydrocarbon (PAH) scaffold to tune the molecular semiconductor properties by editing the oxidation state of the S-atoms. Chemical oxidation of *peri*-thiaxanthenothioxanthene with H₂O₂ led to the relevant sulfoxide and sulfone congeners, whereas electrooxidation gave access to sulfonium-type derivatives forming crystalline mixed valence (MV) complexes. These complexes depicted peculiar molecular and solid-state arrangements with face-to-face π - π stacking organization. Photophysical studies showed a widening of the optical bandgap upon progressive oxidation of the S-atoms, with the

bis-sulfone derivative displaying the largest value ($E_{00} = 2.99$ eV). While *peri*-thiaxanthenothioxanthene showed reversible oxidation properties, the sulfoxide and sulfone derivatives mainly showed reductive events, corroborating their *n*-type properties. Electric measurements of single crystals of the MV complexes exhibited a semiconducting behavior with a remarkably high conductivity at room temperature (10^{-1} – 10^{-2} S cm⁻¹ and 10^{-2} – 10^{-3} S cm⁻¹ for the O and S derivatives, respectively), one of the highest reported so far. Finally, the electroluminescence properties of the complexes were tested in light-emitting electrochemical cells (LECs), obtaining the first S-doped mid-emitting PAH-based LECs.

Introduction

Replacing the carbon atoms with isostructural atoms at given positions is a functionalization strategy to tailor the chemical, optoelectronic, and self-assembly properties of molecular and macromolecular polycyclic aromatic hydrocarbons (PAHs).^[1–3] While B,^[4–7] N^[8–10] and P^[11–15] heteroatoms can replace both the core and peripheral C(sp²) atoms, the use of chalcogen atoms is fundamentally restricted to the doping of the peripheries. Noticeable examples include O-,^[16] S-,^[17–19] Se-^[20–22] and Te-doped^[23,24] structures. In recent years, our group became interested in the development of novel O-doped PAHs.^[25–27] In

particular, we became interested in the O-containing congener of anthanthrene, *peri*-xanthenoxanthene (PXX),^[28–31] and developed synthetic strategies to prepare molecular ribbons^[32,33] and mono/diimide^[34,35] derivatives. It was observed that the insertion of O-atoms induces a rising of the highest occupied molecular orbital (HOMO) energy level, displaying *p*-type behavior.^[29,31,36,37]

The oxidation of the pyrano-derived aromatics readily gives access to stable pyrylium cations, featuring significantly red-shifted UV-vis absorption spectra when compared to their neutral forms.^[38,39] However, the narrow multivalency space of the oxygen atom limits the structural and optoelectronic

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 Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202203115>

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variabilities that one can access through chemical editing of the heteroatom valency (i.e., through oxidation). In contrast, the other chalcogen atoms, S, Se, and Te atoms, feature a large multivalency space (from II to VI).^[40] Thus, we conjectured that peri-thioxanthanthrene (4^H), the S-doped congener of PXX in which the O-atoms are replaced by S-atoms,^[41,42] could be an ideal structural motif to engineer PAHs, whose optoelectronic properties are tailored by tweaking the chalcogen-atoms valency through oxidation (Figure 1). In particular, it is expected that mono- and di-oxidation of the S-atoms could be reflected in the widening of the molecular HOMO-LUMO gap, rising of the ionization potential and inducing a perturbation of the conformational properties that rule the solid-state organization. Indulging this line of thought, herein we report on the preparation, solid-state organization, and optoelectronic properties of the sulfoxide, sulfone, and sulfonium derivatives of peri-thioxanthanthrene (PTXTX). Building on the same synthetic strategy, the synthesis of the Se-congener periselenoxanthanthrene (PSXSX) is also reported. The electrical and electroluminescent behaviors of the most relevant and chemically inert derivatives have been analyzed and the first mid-energy emitting S-doped PHA-based light-emitting electrochemical cells (LECs) have been realized.

Results and Discussion

Synthesis and structural characterization of the sulfoxide and sulfone derivatives

Dibromo-1,1'-binaphthalene **1** was reacted with *n*-BuLi in the presence of TMEDA followed by the addition of (MeS)₂,^[43] providing intermediate dimethylthiobinaphthalene **2^H** in 79% yield (Scheme 1). Subsequent bromination with Br₂ afforded compound **2^{Br}** in 90% yield that, under Kumada cross-coupling conditions with OctylMgBr, afforded derivative **2^{Oct}** (70%).

Oxidation of molecules **2^H** and **2^{Oct}** with H₂O₂ in CH₃COOH/CHCl₃ quantitatively afforded desired disulfoxide derivatives **3^H**

and **3^{Oct}** as diastereomeric mixtures.^[18] Friedel-Craft cyclization in TfOH, followed by demethylation reaction in a pyridine/H₂O mixture,^[44,45] gave derivatives **4^H** and **4^{Oct}** as orange solids in 35% and 29% yield, respectively. Subsequent oxidation of **4^H** and **4^{Oct}** in CH₃COOH/CHCl₃ with six and eight eq. of H₂O₂ afforded sulfoxides (±)-**5^H** and (±)-**5^{Oct}** in 50% and 59% yield, respectively. When 20 equiv. of H₂O₂ were used, disulfoxide **6^H** was instead obtained as a mixture of *trans* (**t-6^H**) and *cis* ((±)-**c-6^H**) isomers in 87% yield. While the *cis* isomer rapidly decomposes on SiO₂, **t-6^H** could be isolated as a pure product. Traces of the sulfone-sulfoxide conjugate were also isolated as confirmed by X-ray diffraction analysis (see the X-ray structure shown in Figure S94, of molecule **11^H**). Despite a few attempts, we could not prepare the sulfone-sulfoxide conjugate selectively and isolate it with sufficient purity under our experimental conditions. When a large excess of H₂O₂ in CH₃COOH is used under reflux conditions for 16 h, molecules **4^H** and **4^{Oct}** oxidize to the disulfones (**7^H** and **7^{Oct}**). While the alkylated derivative **7^{Oct}** could be isolated (48% yield) and characterized, unsubstituted compound **7^H** is insoluble in common organic solvents. Prompted by these results, we also explored the possibility to extend this synthetic strategy to the preparation of the Se-congener, PSXSX, and its oxidized derivatives. Thus, the reaction of **1** with *n*-BuLi and TMEDA followed by the addition of (MeSe)₂ gave dimethylselenobinaphthalene **8** in 65% yield (Scheme 1). Oxidation with H₂O₂ in CH₃COOH/CHCl₃ quantitatively afforded selenoxide **9** as a mixture of diastereoisomers. Friedel-Craft cyclization with neat TfOH followed by demethylation gave targeted Se-doped anthanthrene **10** (PSXSX) as a poorly soluble solid in 44%. Unlikely PTXTX, attempts to oxidize PSXSX to either its selenoxide or selenium dioxide derivatives proved to be unsuccessful and gave decomposition products. All molecules were characterized by NMR techniques, HR-MS spectrometry, and, when possible, single-crystal X-ray diffraction. Due to its low solubility, derivative **7^H** was characterized only by mass and X-ray analyses.

Crystallization of compounds **4^H**, **4^{Oct}**, **5^H**, **t-6^H**, **7^H**, **7^{Oct}**, and **10** for X-ray diffraction analysis were successful (Figure 2), while

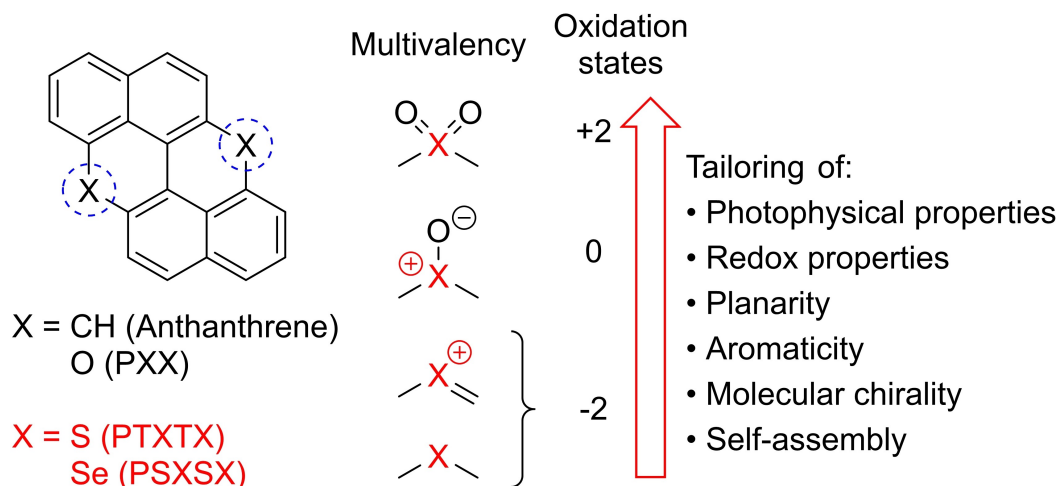
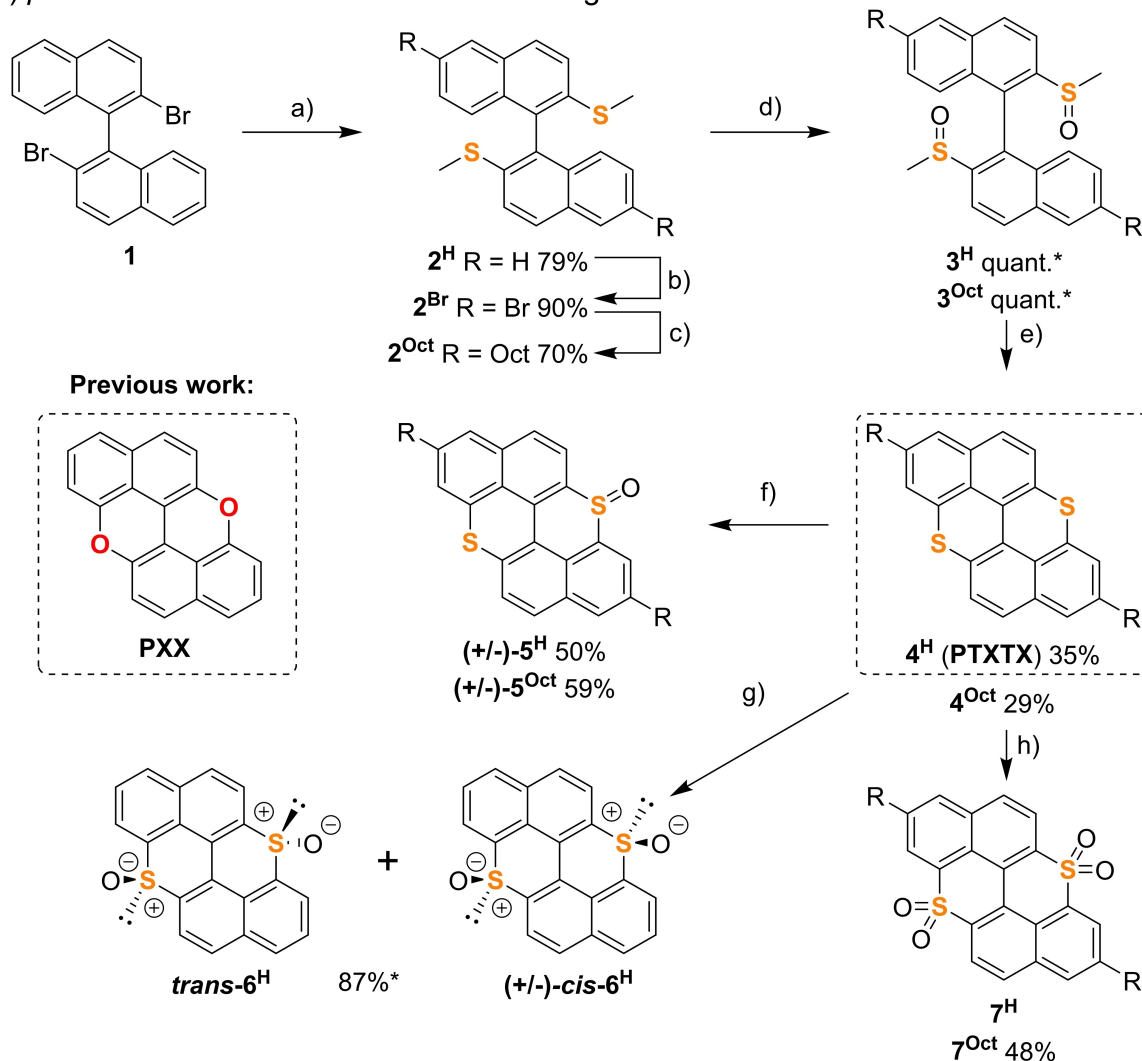
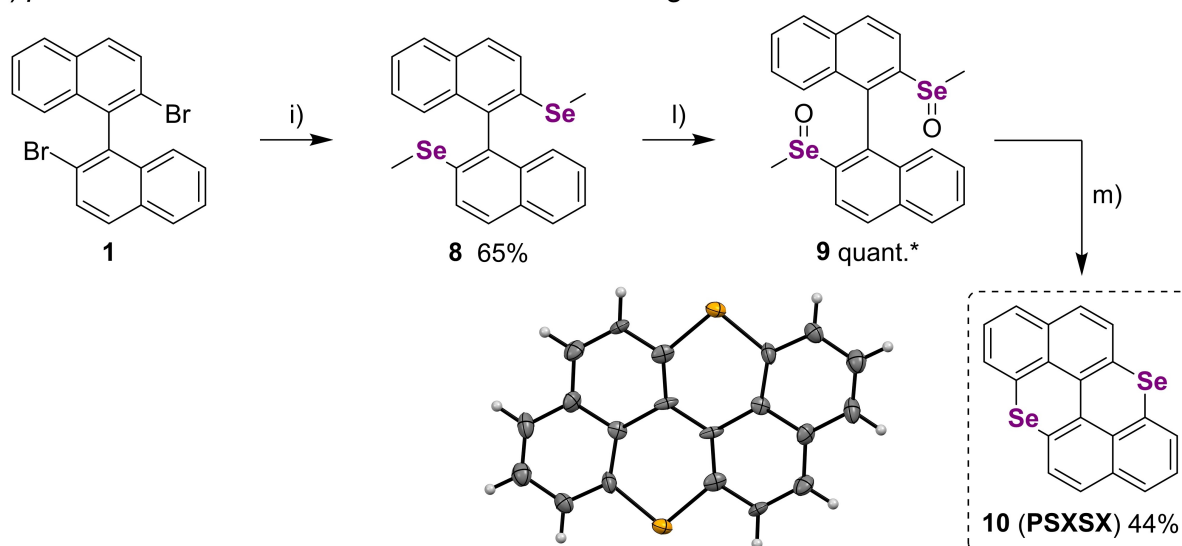


Figure 1. S and Se-doped anthanthrenes and their multivalent species.

a) *peri*-thioxanthenthioxanthene scaffoldingb) *peri*-selenoxanthenoselenoxanthene scaffolding

Scheme 1. a) 1. *n*-BuLi, TMEDA, THF, -94°C to 0°C , under N_2 , 1 h; 2. Me_2S_2 , -94°C to rt, under N_2 , overnight; b) Br_2 , CH_2Cl_2 , under N_2 , 0°C to rt, overnight; c) OctMgBr, THF, $[\text{Pd}(\text{dppf})\text{Cl}_2]$, under N_2 , reflux 2.5 h, rt, overnight; d) H_2O_2 , CH_3COOH , CHCl_3 , rt, 5 h; e) 1. TfOH, under N_2 , rt, 24 h; 2. Pyridine/ H_2O , 100°C , 1 h; f) H_2O_2 , CH_3COOH , CHCl_3 , rt, 6 h; g) H_2O_2 , CH_3COOH , CHCl_3 , rt, 24 h; h) H_2O_2 , CH_3COOH , reflux, overnight; i) 1. *n*-BuLi, TMEDA, THF, -78°C , 1 h, under N_2 ; 2. Me_2Se_2 , under N_2 , from -78°C to rt, overnight; j) H_2O_2 , AcOH, CHCl_3 , rt; m) 1. TfOH, 80°C , under N_2 , overnight; 2. Pyridine, 100°C , under N_2 , overnight. *yield of the diastereoisomeric mixture. X-ray structure of molecule 10; space group: $\text{P}2_1/\text{c}$; atom colors: orange Se, grey C.

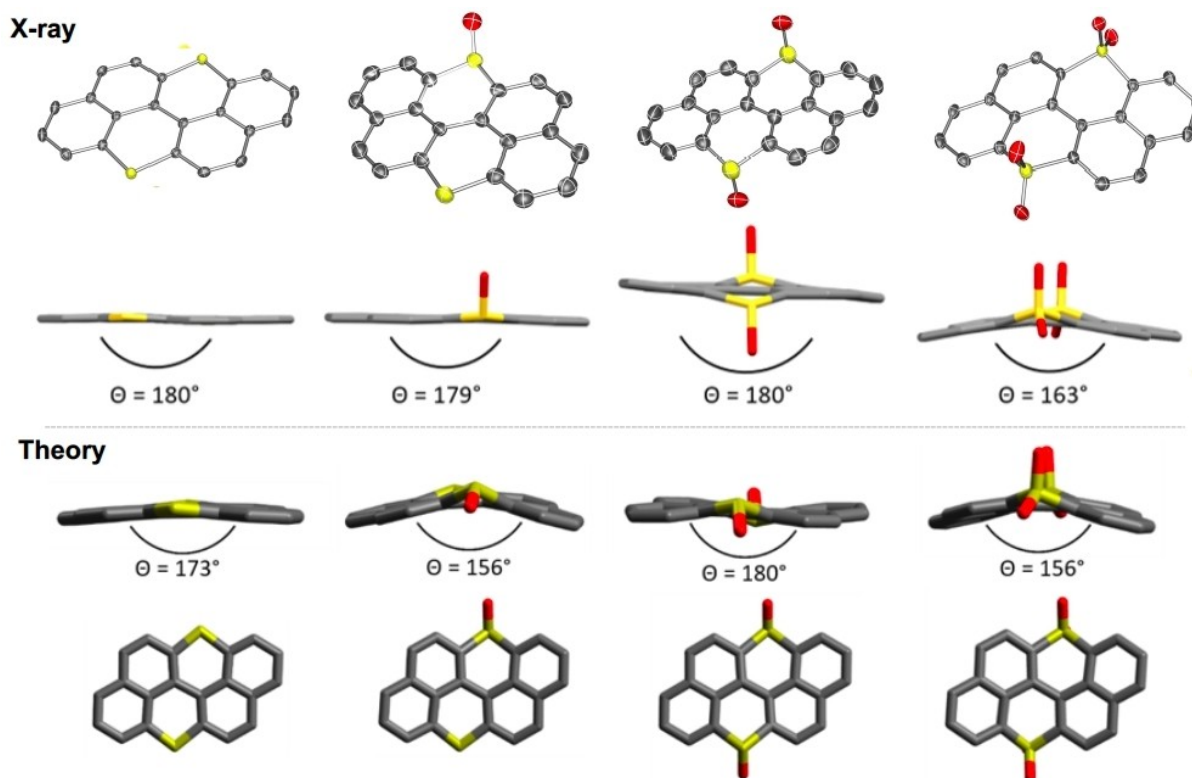


Figure 2. Crystal (top) and calculated at the B3LYP/cc-pVTZ level of theory (bottom) structures for PAHs 4^H , 5^H , $t\text{-}6^H$ and 7^H . Space groups for crystals are: $P2_1/c$, $P2_12_12_1$, $P2_1/c$, and $P-1$, respectively. The Θ value is the angle that is formed between the planes comprising the two naphthalenyl rings. Atom colors: red O, yellow S, grey C. Theoretical calculations in vacuum reported consistent conformations to those observed experimentally for molecules 4^H , 5^H , 7^H , and $t\text{-}6^H$.

all attempts to obtain crystals of $c\text{-}6^H$ failed. Single crystals of 4^H were prepared by slow diffusion of EtOH vapors into CH_2Cl_2 , giving rise to two polymorphic crystals: yellow plates (Figure S85A, polymorph A) and red needles (Figure S86A, polymorph B). The polymorphs show similar bonds lengths and angles within the experimental errors ($d_{\text{C-S}} = 1.741(2) \text{ \AA}$; C-S-C angle = $103.9(1)^\circ$ for the plates and $d_{\text{C-S}} = 1.739(5)\text{--}1.740(5) \text{ \AA}$; C-S-C angle = $104.0(2)\text{--}104.1(2)^\circ$ for the plates vs. $d_{\text{C-O}} = 1.389(1)\text{--}1.391(1) \text{ \AA}$ and C-O-C angle = $118.80(8)^\circ$ for PXX).^[46] A lamellar-type organization driven by the interdigitation of the octyl chains was observed instead for the X-ray structure of molecule 4^{Oct} (Figure S87). Crystals suitable for X-ray for Se-congener **10** were obtained by hot crystallization from a 1:1 toluene and hexane mixture (Scheme 1). Similarly to molecule 4^H , the naphthyl rings are co-planar. The C-Se-C angle is $100.1(6)^\circ$, which is significantly lower than the C-S-C and C-O-C angles measured for PTXTX ($103.9(1)^\circ$) and PXX ($118.80(8)^\circ$). The length of C-Se bonds in **10** is $1.87(1)\text{--}1.88(1) \text{ \AA}$, which is longer than the corresponding C-S and C-O bonds in PTXTX ($1.741(2) \text{ \AA}$) and PXX ($1.389(1)\text{--}1.391(1) \text{ \AA}$). The molecules arrange in $\pi\text{-}\pi$ stacks (3.526 \AA) organized in a slip-type fashion, similar to the yellow-plate polymorph of PTXTX. Each stack interacts intercolumnary through Se \cdots Se contacts ($d_{\text{Se}\cdots\text{Se}} = 3.658(2) \text{ \AA}$).

Crystals of 5^H were obtained by hot recrystallization from CH_3CN . The X-ray structure confirmed the presence of sulfoxide

moiety (Figure 2). Notably, the C-S bond lengths of the thioether functions ($d_{\text{C-S}} = 1.735(6)\text{--}1.739(6) \text{ \AA}$) are consistent with that observed for molecule 4^H , whereas those of the sulfoxide moiety are $1.772(6) \text{ \AA}$ and $1.760(6) \text{ \AA}$. Single crystals of $t\text{-}6^H$ and 7^{Oct} were grown by hot crystallization from DMSO. The X-ray analysis of $t\text{-}6^H$ confirmed the *trans* disposition of the sulfoxide groups, whereas 7^H showed the full oxidation of both thioether functions to sulfones (Figure 2). Notably, $t\text{-}6^H$ displays a *saddle*-type distortion, with the two O-atoms situated in *pseudo-equatorial* positions. On the other hand, disulfone 7^H adopts a slightly bent V-type conformation where two of the O-atoms are placed in *pseudo-axial* and two in *pseudo-equatorial* positions (Figure 2). In this structure, the C-S bond lengths are $1.745(2)\text{--}1.748(2) \text{ \AA}$ and $1.749(3)\text{--}1.751(2) \text{ \AA}$ and are very similar to those observed in 5^H ($d_{\text{C-S}} = 1.735(6)\text{--}1.739(6) \text{ \AA}$). Notably, in all the oxidized derivatives, a network of weak H-bonding interactions is established between the O-atoms and the aromatic C-H (Figure S88, S90, and S91), which is thought to be responsible for their low solubility. Crystals of derivative 7^{Oct} were grown from slow diffusion of hexane into toluene. Notably, plate- and rod-like crystals belonging to the $C2/c$ and $P2_1/c$ space groups, respectively, were obtained (Figure 3 and Figure S92). When looking at the X-ray structures of 7^{Oct} in the $P2_1/c$ crystals, one can notice the disulfone framework adopting an *anti*-type conformation (*anti*- 7^{Oct}), in which the two *pseudo-axial* and *pseudo-equatorial* O-atoms are *anti* (Figure 3). On the

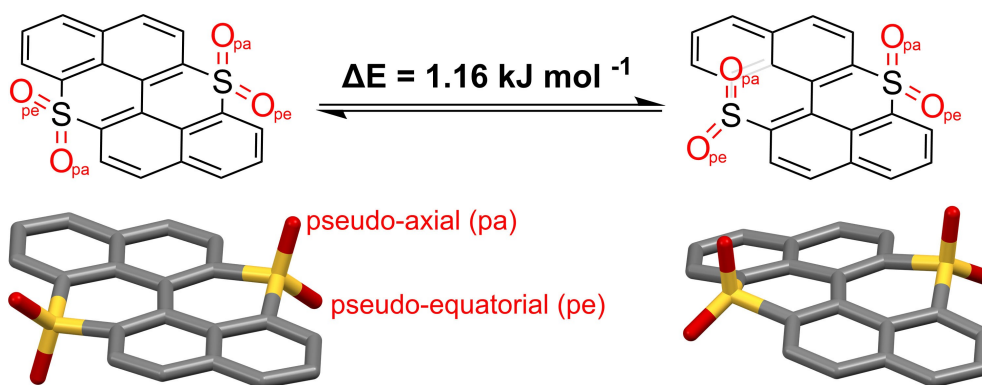


Figure 3. Above: *anti-7^{Ooct}* *syn-7^{Ooct}* conformers (ΔE estimated by DFT calculations from the optimized structures in vacuum at the B3LYP/cc-pVTZ level of theory). Below: X-ray structures of *7^{Ooct}* in polymorphs *P2₁/c* and *C2/c* as obtained by slow diffusion of hexane vapors into a toluene solution containing *7^{Ooct}* (the octyl chains were not included in the calculations and have been omitted for clarity from this figure). Atom colors: red O, yellow S, grey C.

other hand, in the *C2/c* polymorph, the *pseudo-axial* and *pseudo-equatorial* O-atoms are in a *syn*-type conformation, *syn-7^{Ooct}* (Figure 3).

The interdigitation of the octyl chains of *syn-7^{Ooct}* in the *C2/c* crystals allows for the entrapment of hexane solvent molecules forming clathrates (Figure 4). Heating of the *C2/c* crystals induces the evaporation of the hexane molecules, leading to a collapse of the clathrate architecture with a consequent formation of *P2₁/c* crystals (Figure S92). In these crystals, an in-plane interdigitation of the aliphatic chains is observed, with a consequent formation of a lamellar-type organization.

Photophysical and electrochemical characterization

The photophysical properties of *4^H*, *5^H*, *t-6^H*, *7^{Ooct}* and **10** were investigated in CH_2Cl_2 and solid state (Table 1, Figure 5). The

absorption and emission spectra of molecule *4^H* are consistent with those of **PXX**.^[26,34,46] The lowest-energy $\pi \rightarrow \pi^*$ transition absorption band of the former is bathochromically shifted ($\lambda_{\text{max}}=500$ nm) compared to that of **PXX** ($\lambda_{\text{max}}=443$ nm). In addition, the presence of the heavier S atoms lessens the oscillator strength of the $S_0 \rightarrow S_1$ transition, broadening and reducing the intensity of the absorption band ($\epsilon_{\text{max}} \approx 7000 \text{ M}^{-1}\text{cm}^{-1}$ and $17000 \text{ M}^{-1}\text{cm}^{-1}$ for *4^H* and **PXX**, respectively).^[42,47] Compared to molecule *4^H*, the oxidations of S-atoms cause a progressive blue shift of the electronic transition energies. The lowest-energy bands of the absorption spectra of oxidized derivatives *5^H*, *t-6^H*, and *7^{Ooct}* are centered at $\lambda_{\text{max}}=458$ nm, 414 nm and 399 nm, respectively (Figure 5). Emission profiles for molecules *4^H*, *5^H*, *t-6^H*, and *7^{Ooct}* (CH_2Cl_2 at rt) mirror the absorption bands with pronounced vibronic substructures (Figure 5). In addition, narrow Stokes' shifts ($\lambda_{\text{em}}=518$, 539, 483, and 430 nm, respectively), moderated photoluminescence

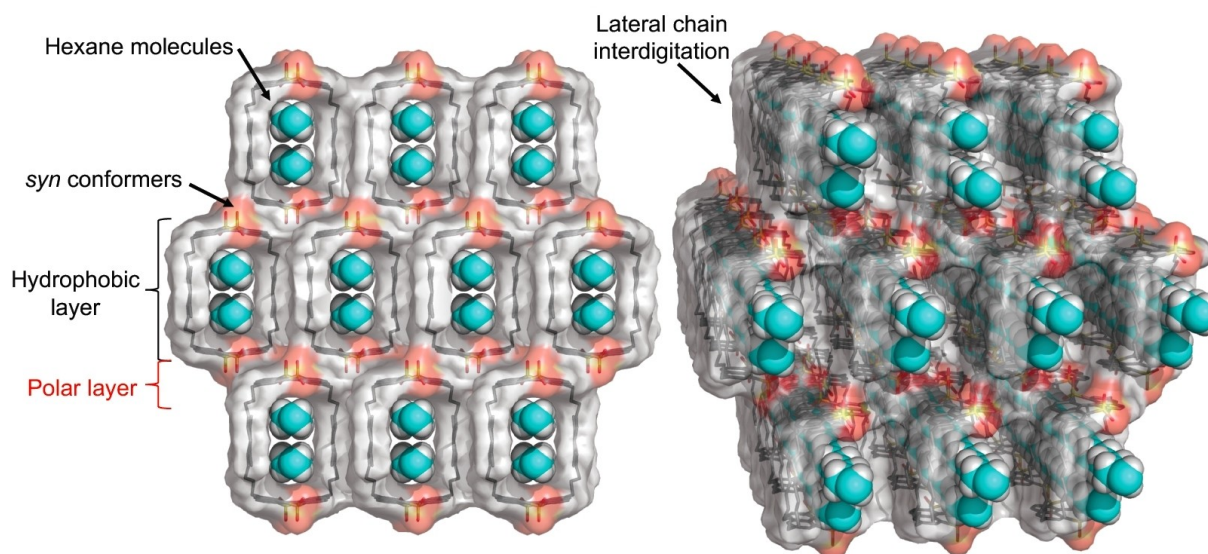


Figure 4. Crystal structure of the organic hydrophobic clathrate made of *syn-7^{Ooct}* encapsulating hexane molecules (cyan-coloured spheres) perfectly aligned with the pore channels. Space group: *C2/c*. Atom colors: red O, yellow S, grey C, green C atoms of the hexane molecules.

Molecule	Absorption λ , nm [ϵ , $M^{-1} \text{cm}^{-1}$]	λ_{max} [nm]	Emission τ [ns] ^[a]	Φ_{em}	E_{00} [eV] ^[d]	Energy Band Gap E_g^T [eV] ^[e]
PXX	443 (17284) ^[34]	450 ^[34]	5.0 ^[34]	0.62 ^{[34][b]}	2.78	3.30
4 ^{Oct}	502 (16728) 470 (17308)	523	6.5	0.48	2.44	2.35 ^[g]
4 ^H	500 (6017) 469 (6367)	518	5.2	< 0.02 ^[b]	2.45 (1.72) ^[f]	3.05
5 ^H	497 (2300) 461 (4017) 421 (2300)	539	11.2	0.22 ^[b]	2.42	3.20
t-6 ^H	420 (6323) 396 (7030)	483	0.6	0.04 ^[b]	2.82	3.37
7 ^{Oct}	400 (9603) 382 (9437)	430	0.7	0.35 ^[c]	2.99	2.89 ^[g]

[a] $\lambda_{\text{exc}} = 450$ or 340 nm. [b] Standard: coumarin 153 in EtOH ($\phi = 0.53$).^[49] [c] 9,10-Diphenylanthracene in CHX ($\phi = 0.97 \pm 0.03$).^[50] [d] Energy calculated at the lowest energy intersection (λ_{int}) between normalized absorption and emission spectra, $E_{00} = 1240.5/\lambda_{\text{int}}$. [e] Calculated bandgap at the B3LYP/cc-pVTZ level of a gas-phased optimized geometry unless otherwise specified. [f] Energy gap between S_0 and T_1 . [g] See Figure S27.

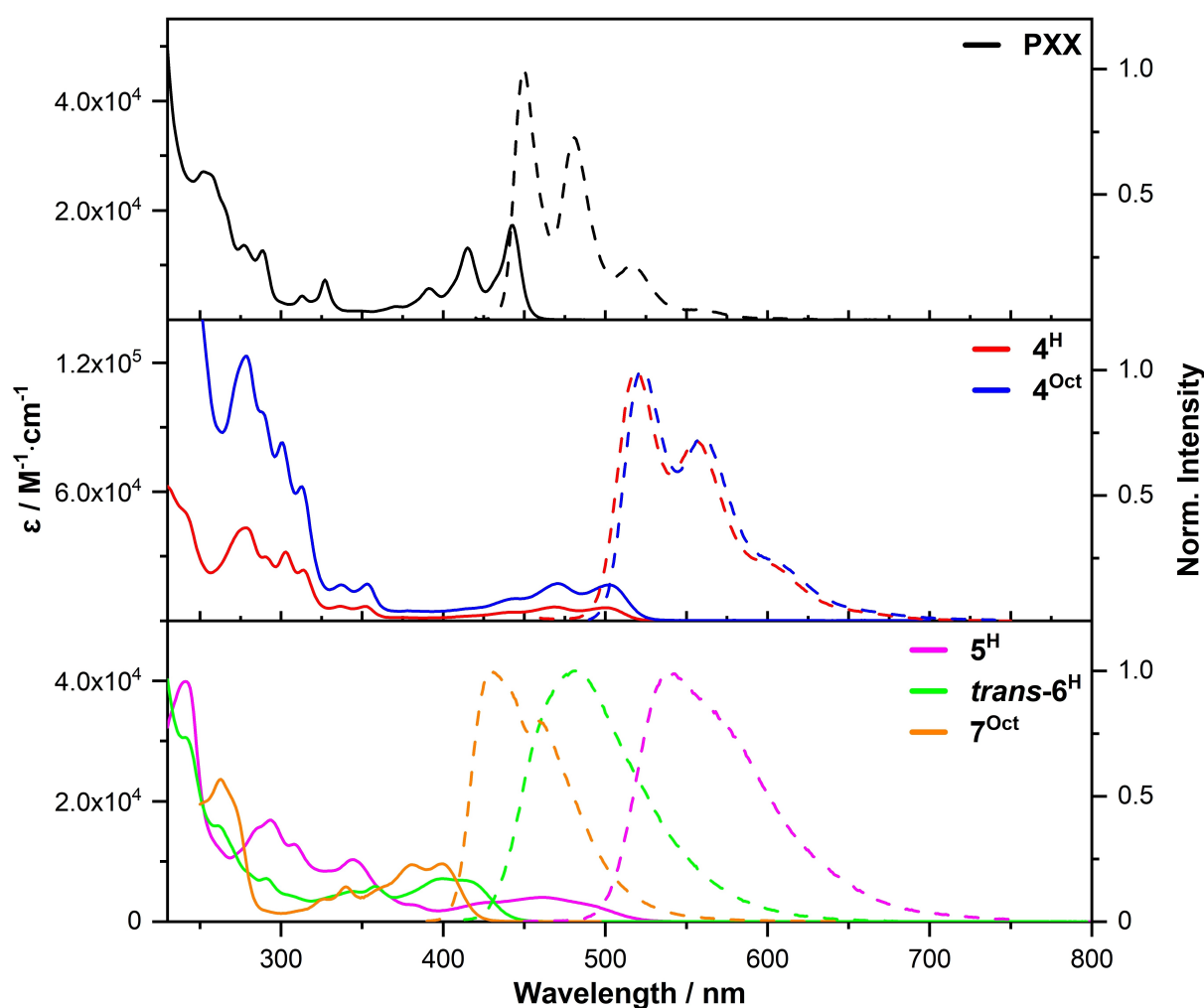


Figure 5. Absorption (—) and fluorescence (---) spectra for PXX (black, $\lambda_{\text{exc}} = 410$ nm), 4^H (red, $\lambda_{\text{exc}} = 450$ nm), 4^{Oct} (blue, $\lambda_{\text{exc}} = 470$ nm), 7^{Oct} (orange, $\lambda_{\text{exc}} = 365$ nm), t-6^H (green, $\lambda_{\text{exc}} = 350$ nm), and 5^H (magenta, $\lambda_{\text{exc}} = 345$ nm) in aerated CH_2Cl_2 at rt.

quantum yields (Φ_{em}) (Φ_{em} = 2%, 22%, 4%, and 35%, respectively) and lifetimes in the nanosecond range (τ = 5.2, 11.2, 0.6, and 0.7 ns, respectively) are observed.

The lower Φ_{em} value of 4^H compared to that of PXX is ascribable to an efficient non-radiative deactivation via triplet population. This hypothesis was confirmed by 1O_2 -sensitisation measurements, showing 1O_2 quantum yields ($\Phi_{rel}(^1O_2)$) of 0.26 and 0.64 for PXX and 4^H , respectively (Figure S22, Table S2). The triplet state population was further verified experimentally by the detection of a phosphorescence peak for molecule 4^H centered at λ = 700–820 nm (τ = 210 μ s) at 77 K, induced by external heavy atom effect in the presence of CH_3I (Figure S20).^[48]

As far as Se-derivative **10** is concerned, we noticed that small impurities of other emissive species were always present in solution, likely deriving from oxidation, preventing us from performing a comprehensive photophysical characterization (Figure S21).

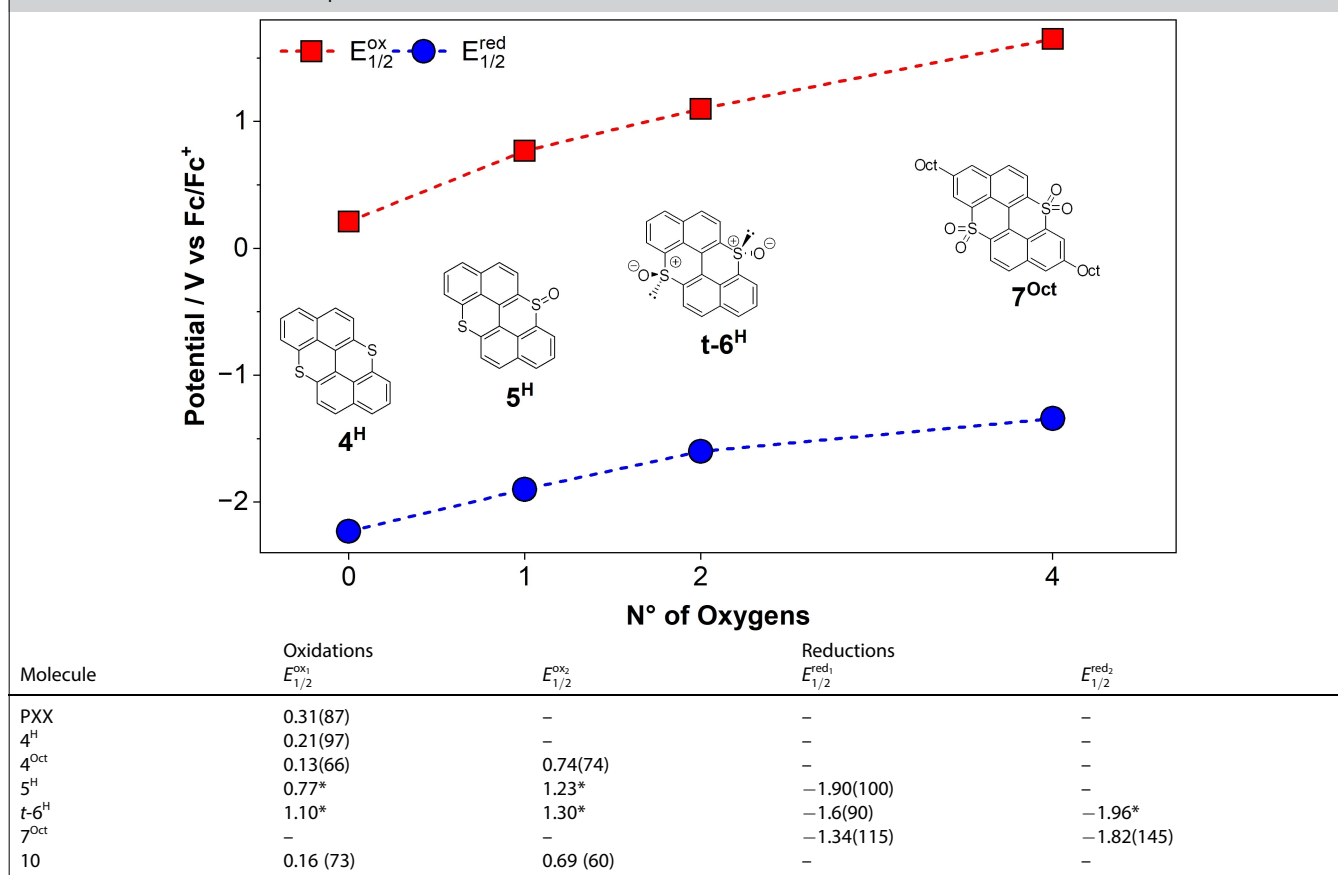
Cyclic voltammetry (CV) measurements were performed to investigate the molecules' redox properties (Table 2, Figure S12–S19). Molecule 4^H possesses a lower oxidation potential ($E_{1/2}^{ox_1}$ = 0.21 V) than PXX ($E_{1/2}^{ox_1}$ = 0.31 V), whereas oxidized derivatives 5^H , $t-6^H$ showed irreversible oxidative events. On the other hand, reversible reduction peaks were observed for 5^H , $t-6^H$ and 7^{Oct} ($E_{1/2}^{red_1}$ = –1.90 V, –1.60 V and –1.34 V, respectively). A

second reduction wave was also observed for derivatives $t-6^H$ and 7^{Oct} at $E_{1/2}^{red_2}$ = –1.96 V (irreversible) and –1.82 V (reversible), respectively. As expected, S-doping enhances the reduction behavior compared to PXX. Orbital energy calculations performed on the optimized geometries in vacuum showed a lowering of the HOMO-LUMO energy bandgap upon substitution of the O with S atoms, along with its widening upon progressive oxidation (Figure S26), confirming both the data obtained from the electrochemical and photophysical studies.

Synthesis and structural characterization of sulfonium-type derivatives

Next, we performed electrooxidation experiments^[38] to grow crystals of sulfonium-type cations of 4^H and oxonium-type references of PXX (Supporting Information, Section 4). Attempts to provide crystals of oxidized species of PSXSX and 7^{Oct} failed. Orthorhombic shiny black crystals containing salts of mixed-valence (MV) complexes for PXX were obtained in a solution of THF with 20% EtOH over a period of ten days (Figure 6). On the other hand, monoclinic black needles containing MV complexes of 4^H were prepared in three days (Figure 7). While PXX electrocrystallizes in an asymmetric unit containing two crystallographically-independent molecules and one ClO_4^- (WARNING:

Table 2. Plot of $E_{1/2}^{ox_1}$ and $E_{1/2}^{red_1}$ vs. the total number of oxygen atoms attached to S. CV data of PXX, 4^H , 4^{Oct} , 5^H , $t-6^H$, 7^{Oct} , **10** in CH_2Cl_2 at rt (scan rate: 0.05 $V s^{-1}$, TBAPF₆ as electrolyte (0.1 M), and Ferrocene as internal reference). Values between brackets represent the peak-to-peak separation of the reversible redox events. *Irreversible peaks.



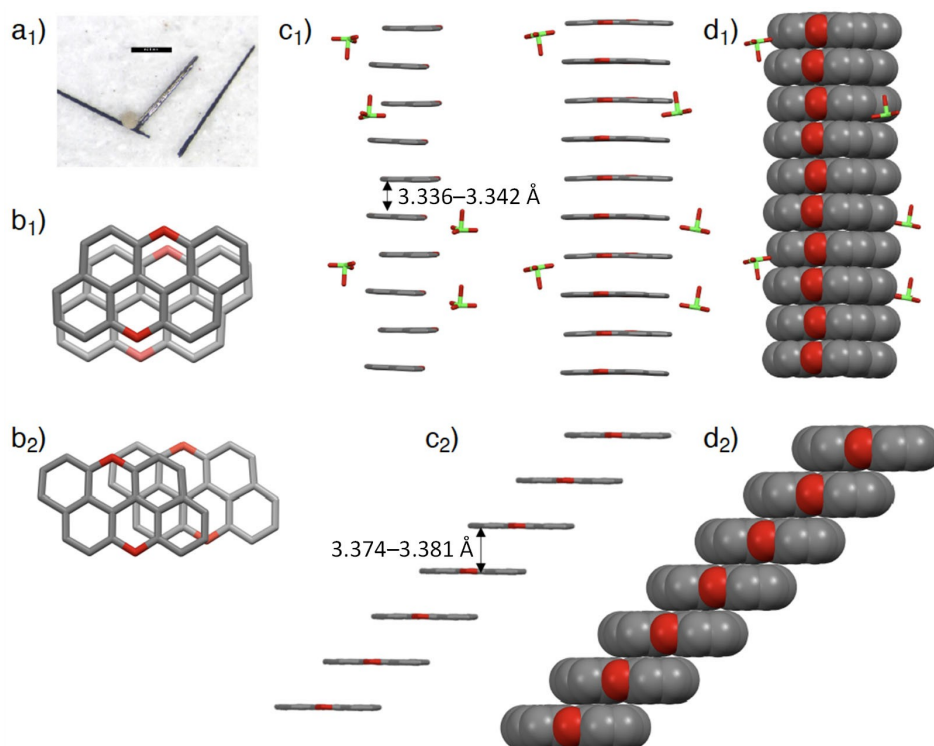


Figure 6. X-ray structures and solid-state organization for MV complexes $(\text{PXX})_2(\text{ClO}_4)_1$ (a1, b1, c1, d1) and reference neutral PXX (b2, c2, d2). a) Morphology of the crystals, b) X-ray structure of the relevant isolated O-doped molecules in their π - π stacking mode. c-d) Solid-state columnar π - π stacks. Atom colors: red O, grey C, green Cl.

precautions need to be taken when dealing with perchlorates as they are potentially explosive), $(\text{PXX})_2(\text{ClO}_4)_1$, the S-doped congener depicts three independent molecules and two ClO_4^- anions, $(4^{\text{H}})_3(\text{ClO}_4)_2$.

Looking at the organization in the solid state of $(\text{PXX})_2(\text{ClO}_4)_1$ (Figure 6b₁–d₁), one can evidence the presence of a columnar arrangement (Figure 6b₁), with an average interplanar spacing of 3.33(7) Å (shortest distance between ring centroids of 3.367(12) Å with a lateral slippage of 0.83 Å). The ClO_4^- counterions are evenly intercalated in between the stacks (Figure 6c₁). Similarly, in the crystal of $(4^{\text{H}})_3(\text{ClO}_4)_2$ (Figure 7b₁–d₁), the molecule solely segregates in pillars of π - π stacks ($d_{\pi-\pi}$ from 3.35 to 3.37 Å, Figure 7c₁), with ClO_4^- anions intercalating between different stacks. In contrast, neutral molecule 4^{H} arranges exclusively from typical herringbone organization in the neutral state (Figure 7b₂–d₂), with the π - π stacks featuring different off-set depending on the polymorph. While in the red needles (polymorph B) the molecules are face-to-face off-set like in graphite-like arrangement (2.80 Å, 3.41 and 3.51 Å, Figure S86), in the yellow crystals (polymorph A) π - π stacks organize in a slip-type fashion (1.79 Å, 3.45 Å, Figure S85).

Electrical characterization of the mixed-valence complexes

Electric investigations of single crystals of both MV complexes $(\text{PXX})_2(\text{ClO}_4)_1$ and $(4^{\text{H}})_3(\text{ClO}_4)_2$ revealed a semiconducting behav-

ior with ohmic I–V curves (a few crystals were measured for each material, see Supporting Information Section 5).^[51] The conductivities (σ) at rt are in the order of 10^{-2} – $10^{-3} \text{ S cm}^{-1}$ for $(4^{\text{H}})_3(\text{ClO}_4)_2$ and 10^{-1} – $10^{-2} \text{ S cm}^{-1}$ for $(\text{PXX})_2(\text{ClO}_4)_1$. The temperature dependence of the conductivity in the range of 150 K and 300 K (Figure 8) can be modeled by considering single activation energy in the Arrhenius plots, with average $E_a = 175 \text{ meV}$ and 70 meV for $(4^{\text{H}})_3(\text{ClO}_4)_2$ and $(\text{PXX})_2(\text{ClO}_4)_1$, respectively (See Supporting Information). Except for TCNQ-TTF co-crystals, and a few examples of MOFs and radicals, generally organic semiconducting materials are insulators or weakly conductive ($\sigma < 10^{-6} \text{ S cm}^{-1}$ at 300 K). If compared to previous organic mixed-valence complexes obtained by us previously with O-doped PAHs,^[38] which featured $\sigma_{\text{ohmic}} = 8.8 \times 10^{-5}$ and $3.7 \times 10^{-3} \text{ S cm}^{-1}$; $\sigma_{\text{non-ohmic}} = 2.4 \times 10^{-4}$ and $5.1 \times 10^{-3} \text{ S cm}^{-1}$, both $(\text{PXX})_2(\text{ClO}_4)_1$ and $(4^{\text{H}})_3(\text{ClO}_4)_2$ MV crystals display one of the best conductivity values for an organic semiconductor to date.

Electroluminescence behavior in LEC

Light-emitting electrochemical cells (LECs) are thin-film lighting devices based on a blend of an electroluminescent material and an ionic electrolyte sandwiched between two air-stable electrodes.^[52–54] They are characterized by a low-cost and easy-to-upscale fabrication process with solution-based techniques (i.e., spray coating, gravure printing), high tolerance towards

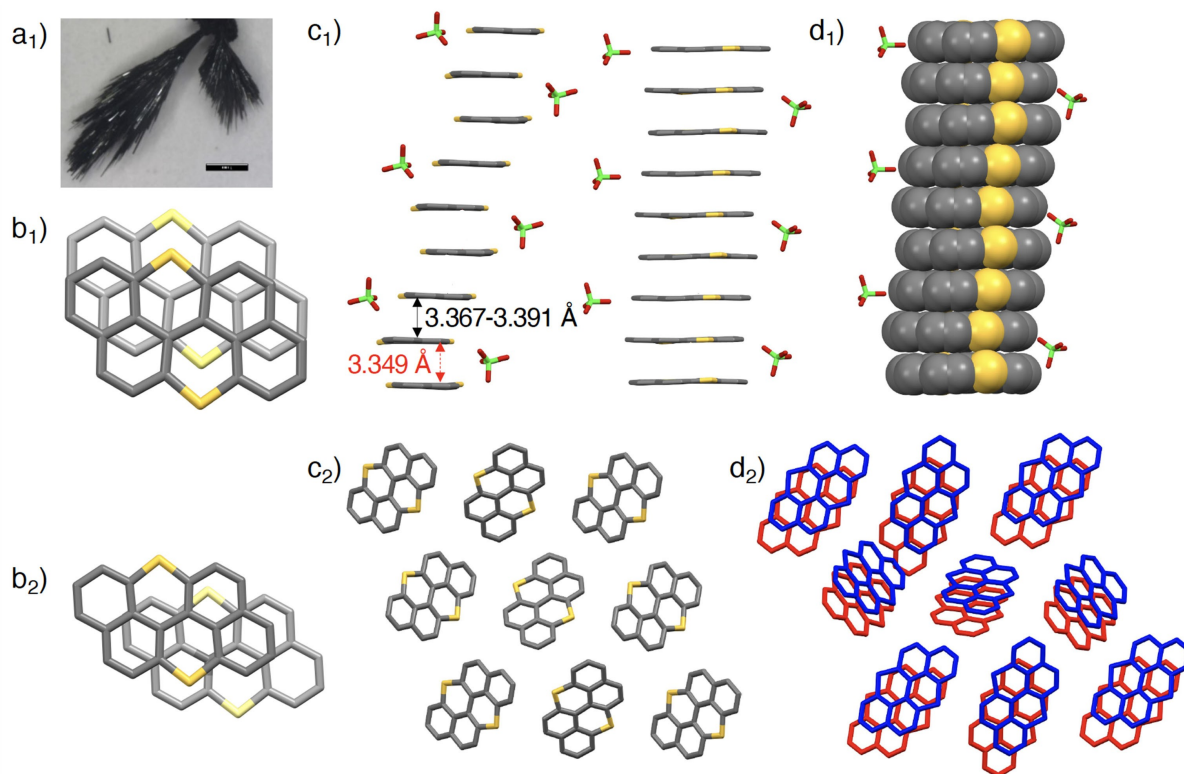


Figure 7. X-ray structures and solid state organization for MV complexes $(4^H)_3(\text{ClO}_4)_2$ (a1,b1,c1,d1) $P2_1/c$ and reference neutral 4^H (b2, c2, d2) $P2_1/c$. a) Morphology of the crystals; b) X-ray structure of the relevant isolated 4^H molecule in a stacking mode, c-d) solid-state columnar π - π stacks. For the MV complexes, two stacking modes between two 4^H molecules were observed. Atom colors: red O, grey C, green Cl, yellow S.

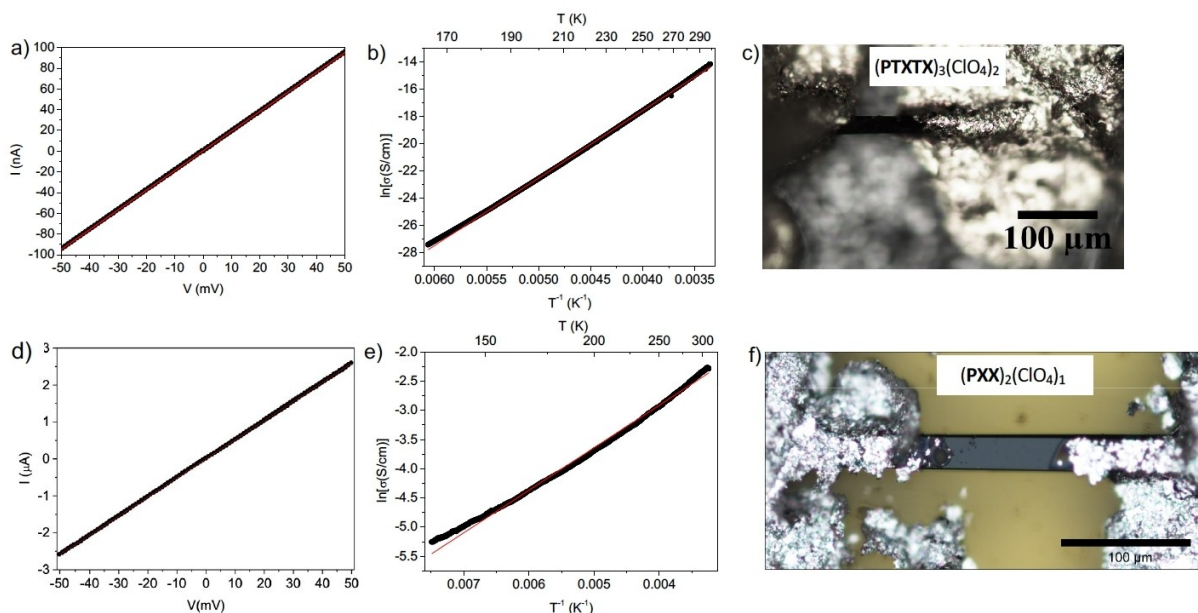
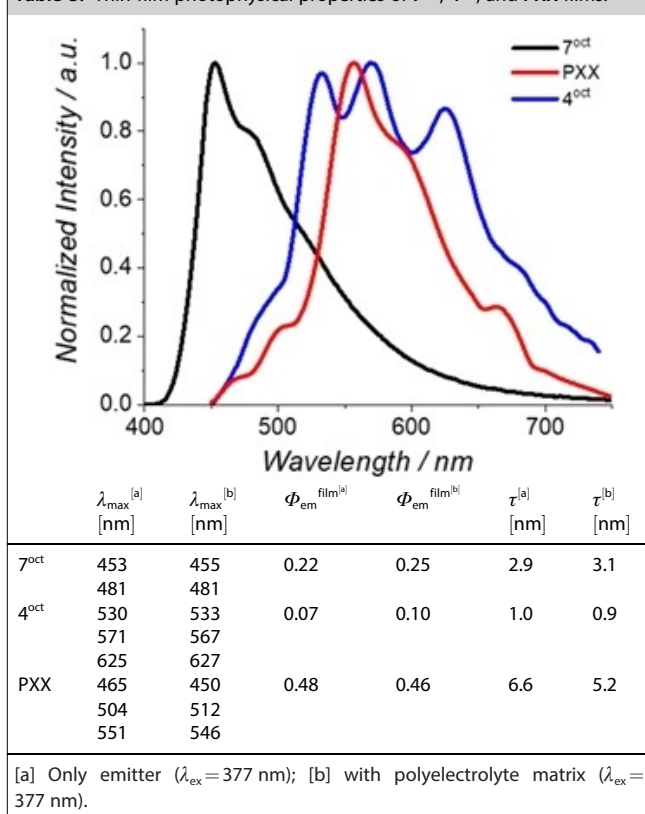


Figure 8. Device and electrical response of crystals of $(4^H)_3(\text{ClO}_4)_2$ (a-c) and $(\text{PXX})_2(\text{ClO}_4)_1$ (d-f). a) and d) I-V curves (•••) at 300 K with the ohmic linear fit (—); for $(4^H)_3(\text{ClO}_4)_2$: ohmic fit ($R^2 = 0.99998$), slope $1.8982 \pm 0.0005 \times 10^{-6} \Omega^{-1}$, y-intercept $2.6 \pm 0.2 \times 10^{-10} \text{ A}$; for $(\text{PXX})_2(\text{ClO}_4)_1$: ohmic fit ($R^2 = 0.99995$), slope $5.169 \pm 0.003 \times 10^{-5} \Omega^{-1}$, y-intercept $4.3 \pm 0.8 \times 10^{-9} \text{ A}$. b) and e) Arrhenius plot of the conductivity vs. temperature (•••) together with the linear fit (—). For $(4^H)_3(\text{ClO}_4)_2$ and $(\text{PXX})_2(\text{ClO}_4)_1$: $E_a = 185.29 \pm 0.02 \text{ meV}$ ($R^2 = 0.99931$) and $E_a = 62.83 \pm 0.07 \text{ meV}$ ($R^2 = 0.99466$), respectively; Top views of the single crystal devices c) and f). The conductivity and activation energy values are referred to the specific devices displayed in c) and f) pictures (more data are reported in the Supporting Information).

the type of electrodes and the active layer thickness, and high versatility with respect to the type of emitters and ionic electrolyte.^[53,54] In this context, PAHs emitters, such as twisted nanographene,^[55] BN-doped coronene,^[56,57] pentacene,^[58] pyrene^[59–62] derivatives, have explored realizing highly performing blue- or deep-red emitting LECs. However, mid-energy emitting S-doped PAH-based LECs have not been realized yet. Considering the yellowish green emission of the PTXTX-type derivatives and their *p*-type semiconducting properties, we conjectured that the unoxidized derivatives of PTXTX (i.e., **4^H** and **4^{oct}**) could be implemented as emissive layers in LECs. Thin films (thickness of ca. 60 nm) were fabricated onto quartz and Indium Tin Oxide (ITO) substrates using a mixture of the emitters and the ionic matrix, namely trimethylolpropane ethoxylate (TMPE) and potassium triflate (KOTf) in a 1:0.10:0.02 ratio (emitter:TMPE:KOTf). While **4^H**, **5^H**, **t-6^H** and **10** did not show enough solubility in common solvents to process thin films via spin-coating, those with **4^{oct}** along with reference PXX and **7^{oct}** were fabricated. Atomic force microscopy (AFM) assays of **4^{oct}** and PXX films showed a homogeneous morphology with root mean square (RMS) roughness of 3 nm (Figure S8).

In contrast, films containing reference **7^{oct}** displayed the presence of aggregates regardless of the efforts to optimize the solvent mixtures, concentrations, ionic matrix composition, and deposition technique. All films showed a similar photoluminescence spectrum to that observed in solution, with less-structured and slightly red-shifted emission bands (**7^{oct}**: $\lambda_{\text{max}} = 453$ nm, with a shoulder at 481 nm, **4^{oct}**: $\lambda_{\text{max}} = 571$ nm with shoulders at 530 and 625 nm, PXX: $\lambda_{\text{max}} = 551$ nm with further peaks at 465 and 504 nm, Table 3). This goes along with photoluminescence quantum yields $\Phi_{\text{em}}^{\text{film}}$ of 0.25 (**7^{oct}**), 0.10 (**4^{oct}**), and 0.46 (PXX) and average excited state lifetimes $\langle \tau \rangle$ in the ns-regime (Table 3). Noteworthy, the thin-film emission profile and properties ($\langle \tau \rangle$ and $\Phi_{\text{em}}^{\text{film}}$) of the emitters are not affected by the presence of the ionic matrix (Figure S9, Table 3). Notably, the emission band shape holds upon increasing the temperature from 77 K to 373 K (Figure S10), suggesting a stable device color at high and low applied currents.^[56,57] Despite the film morphology, the electroluminescent behavior of **7^{oct}**, **4^{oct}**, and PXX was studied in LECs built as ITO/PEDOT:PSS (90 nm)/PXX, **7^{oct}** or **4^{oct}**:TMPE:KOTf 1:0.10:0.02 (60 nm)/Al (90 nm). They were first tested using repetitive L-I-V (luminance-current intensity-voltage) scans at a speed of 300 mV s⁻¹ (Figure 9). As expected from the electrochemical assays, **7^{oct}**-based devices did not show any electroluminescence responses (Figure S11), as the exciton formation is strongly hindered by the lack of oxidation processes. This contrasts with previous works on phenothiazine-based LECs, in which the oxidized derivative shows a similar blue-shifted emission band, but a suitable redox behavior for LECs.^[63] **4^{oct}**-based and PXX-based devices showed a similar charge injection behavior with a significant electroluminescence response, reaching maximum luminance values of 10 cd m⁻² and 75 cd m⁻², respectively, which are in line with the $\Phi_{\text{em}}^{\text{film}}$ values of the films (Table 3). The electroluminescence responses correspond to a broad emission band centered at 494 nm and 537 nm for PXX and **4^{oct}** (Figure 9) respectively, featuring an overall chromaticity similar to that of the photo-

Table 3. Thin-film photophysical properties of **7^{oct}**, **4^{oct}**, and PXX films.



luminescence outputs of the films and solutions (i.e., green and green-yellow responses with x/y CIE of 0.31/0.52 and 0.36/0.52, respectively). Finally, the electroluminescence spectra do not change upon increasing the applied bias and under repetitive LIV scans (Figure 9), suggesting good stability upon charge injection.

The devices were measured at different pulsed currents (1,000 Hz and 50% duty cycle) of 10 and 20 mA (Table 4 and Figure 10). Both devices show the typical LEC behavior with respect to a high initial applied voltage that rapidly drops due to the formation of electrical double layers at the electrode surfaces leading to an enhanced charge injection process. At this stage, the applied voltage remains in a plateau regime, indicating that the layers are free of pin-hole or black-spot formations (electrochemical damage) related to irreversible device degradation.^[52] Finally, the luminance enhances upon

Table 4. PXX- and **4^{oct}**-based LECs measured at different pulsed currents.

Device	PC ^[a] [mA]	Luminance _{max} ^[b] [cd m ⁻²]	Average Voltage [V]	$t_{1/2}$ ^[c] [h]	E_{tot} ^[d] [mJ]	Eff ^[e] (cd/A)
PXX	10 mA	40.1	2.7	0.3	31.0	0.08
PXX	20 mA	74.2	3.2	0.2	36.5	0.07
4^{oct}	10 mA	9.4	2.6	3.2	82.6	0.02
4^{oct}	20 mA	17.3	2.7	2.2	79.4	0.01

[a] PC: pulsed current. [b] Maximum luminance. [c] Time to reach 50% of the initial luminance. [d] Total emitted energy. [e] Power efficiency.

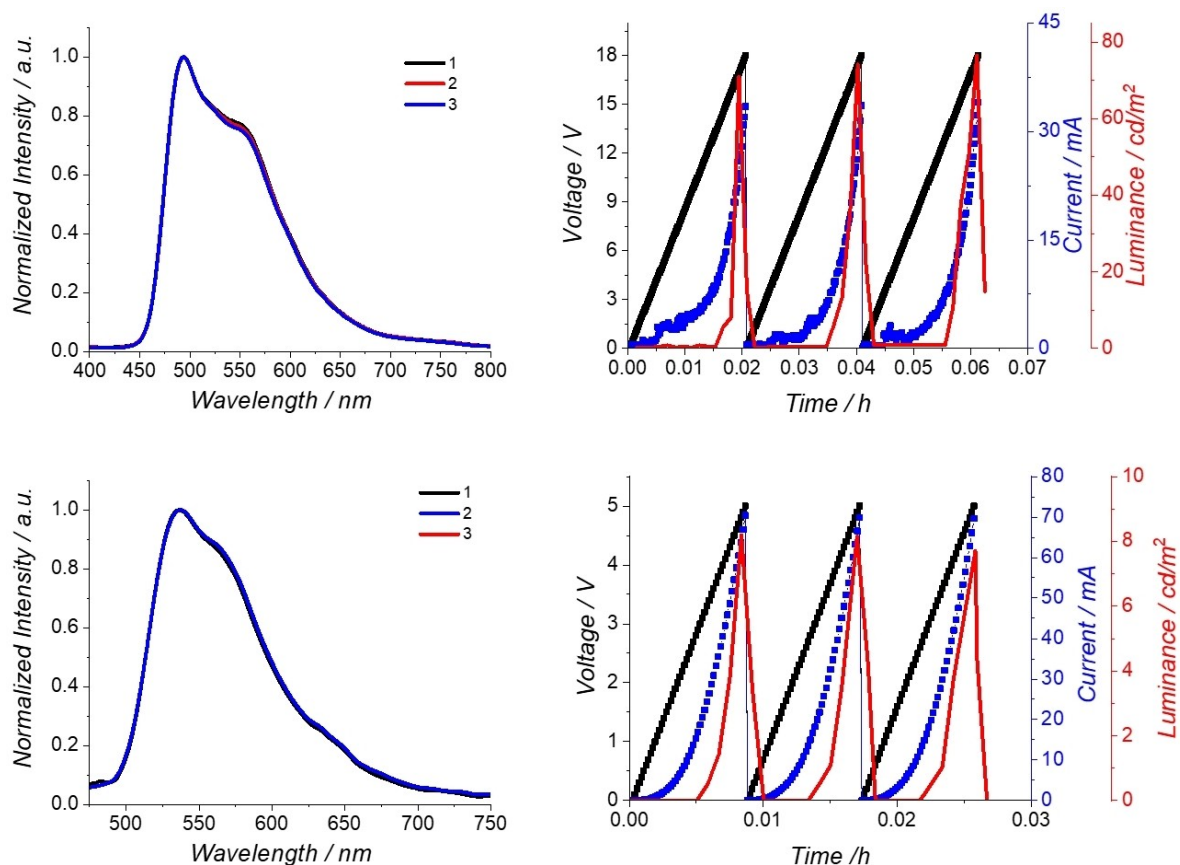


Figure 9. Electroluminescence spectra at 5 V upon repetitive L-I-V scans (see legend) and voltage, current and luminance in repetitive L-I-V scans (right) of PXX- (top) and 4^{oct}-based (bottom) LECs.

the formation of electric double layers (EDLs), reaching the maximum values followed by a quick exponential decay.

Overall, the devices with PXX show good performances with a maximum luminance of ca. 40 and 75 cd m⁻² associated with an average efficacy of 0.1 cd/A at 10 and 20 mA, respectively.

As expected from the reduced Φ_{em}^{film} 4^{oct} films, these devices showed lower luminance values of ca. 10 and 17 cd m⁻² along with lower efficiencies (Table 4). Finally, the device stability of a few hours is similar for both emitters. While these devices are the first examples of mid-emitting S-doped PAH-based LECs, their performance is also comparable to state-of-art green-emitting LECs based on small molecules (e.g., efficiency of 0.1–2 cd/A, and stability, when measured of only a few hours),^[56,60,64–67] attributed to unbalanced charge injection. Considering that both 4^{oct} and PXX compounds possess a strong *n*-type character, unbalanced charge injection and growing of the doped region must be present. This prompted us to conclude that the neutral emitting zone in the *p-i-n* junction is established close to the metal cathode, leading to a prominent exciton quenching and a poor light out-coupling.^[68]

Conclusions

This paper reports a comprehensive study on *peri*-thioxantho-thioxanthenes as novel semiconducting PAHs. The chemical oxidation of 4^H with H₂O₂ gave access to the relevant mono- and di-sulfoxides and sulfone derivatives, whereas electro-oxidation yielded sulfonium-type derivatives as mixed-valence (MV) architectures. Se-doped analog PSXSX was also prepared following the same synthetic approach, but could not be selectively oxidized to provide the selenoxide or selenium dioxide derivatives. The relevant oxidized species were characterized by X-ray crystallography, which revealed peculiar conformational properties in the solid state. Photophysical studies showed that a widening of the optical bandgap could be achieved upon progressive oxidation of the S-atoms, with the bis-sulfone derivative depicting the most significant value. While non-oxidized PTXTX displayed *p*-type properties, the oxidized products expressed an *n*-type behavior as indicated by reversible reductive processes. Electric measurements of single crystals of MV salts of the oxonium- and sulfonium-type derivatives, exhibited a semiconducting behavior with very high conductivity at room temperature (10⁻¹–10⁻² S cm⁻¹ and 10⁻²–10³ S cm⁻¹, respectively). Finally, integrating the PTXTX-based derivatives as emissive materials into LECs led to the first mid-

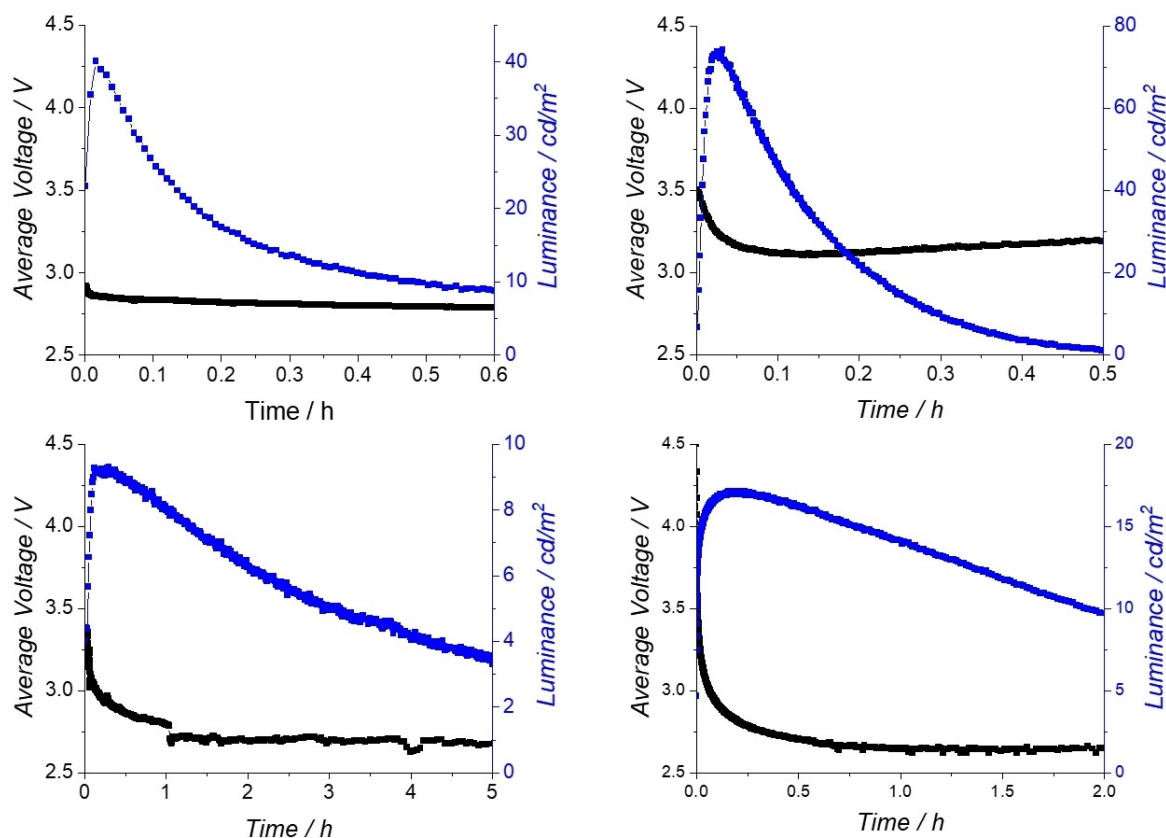


Figure 10. Average voltage and luminance over time of PXX- (top) and 4^{ac}- (bottom) based LECs driven at pulsed 10 mA (left) and 20 mA (right).

emitting devices with performances similar to the state-of-art small molecule-based LECs.^[56,60,65,66,69,70]

Experimental Section

Chemicals were purchased from Sigma Aldrich, Acros Organics, Alfa Aesar, Apollo Scientific, TCI, and Fluorochem and were used as received. Solvents were purchased from Sigma Aldrich, while deuterated solvents from Eurisotop. Dry THF and CH₂Cl₂ were prepared as needed by drying HPLC grade solvents using a Braun MB SPS-800 solvent purification system. Nuclear magnetic resonance spectra were recorded on a Bruker Fourier 300 MHz spectrometer equipped with a dual (¹³C, ¹H) probe, a Bruker AVANCE III HD 400 MHz NMR spectrometer equipped with a Broadband multinuclear (BBFO) SmartProbe™ or a Bruker AVANCE III HD 500 MHz Spectrometer equipped with Broadband multinuclear (BBO) Prodigy CryoProbe. Infrared spectra were recorded on a Shimadzu IR-Affinity 15 FTIR spectrometer in ATR mode with a diamond mono-crystal. High-resolution ESI mass spectra were performed on a Waters LCT HR time of flight mass spectrometer in positive ion mode or in a Waters GCT Premier micromass time of flight spectrometer. High resolution APCI mass spectra were performed on a Waters LCT Premier quadrupole time of flight mass spectrometer operating in atmospheric pressure chemical ionization mode.

Computational details: Calculations and geometry optimizations were carried out using S3 Gaussian 09 including the D01 revision at the B3LYP/cc-pVTZ level of theory. The AICD surfaces have been

calculated using AICD software, developed by Herges and Geuenich.

Synthesis of 2^H: To a solution of 2,2'-dibromonaphthalene (4.0 g, 9.7 mmol) in dry THF (130 mL) TMEDA (3.2 mL, 22 mmol) was added under N₂. *n*-BuLi (1.6 M solution in hexanes) (14.7 mL, 23.3 mmol) was added dropwise at −96 °C and the reaction mixture stirred for 1 h. To the green slurry which formed (MeS)₂ (4.4 mL, 49 mmol) was added at −96 °C, and the yellow mixture was stirred overnight while allowed to slowly return back to rt. Water (50 mL) was added and the mixture extracted with CH₂Cl₂ (3×50 mL). The organic phase was dried with MgSO₄, filtered and concentrated in vacuo with a liquid N₂ trap. The crude was purified through silica gel chromatography (petroleum ether/CH₂Cl₂, 4:1) to give 2^H as a white solid (2.76 g, 82%).

M.p.: 182–183 °C; IR (ATR) ν (cm⁻¹): 3051, 2980, 2914, 1616, 1580, 1557, 1499, 1421, 1335, 1310, 1258, 1211, 1200, 1159, 1132, 1117, 1057, 1024, 951, 943, 856, 800, 777, 772, 745, 737, 691, 669, 610, 559; ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.01 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.41 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 2H), 7.25 (ddd, *J* = 8.5, 6.8, 1.3 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 2.44 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 136.7, 132.7, 132.6, 131.5, 129.0, 128.3, 127.1, 125.3, 125.0, 132.3, 15.9; HRMS (ES⁺): *m/z* [M + H]⁺ calcd for (C₂₂H₁₉S₂): 347.0928; found 347.0928.

Synthesis of 2^{Br}: To a solution of compound 2^H (1.00 g, 2.89 mmol) in dry CH₂Cl₂ (10 mL) a bromine solution was added dropwise (0.4 mL, 7.8 mmol of bromine in 9.6 mL of dry CH₂Cl₂) at 0 °C, under N₂. The mixture was stirred overnight while allowed to slowly reach rt. The reaction mixture was quenched by the addition of saturated Na₂S₂O₃ solution (20 mL) and extracted with CH₂Cl₂ (3×50 mL). The

combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated in vacuo. The crude was purified by silica gel chromatography (petroleum ether/ CH_2Cl_2 5:1) to afford 2^{Br} as a white solid (1.31 g, 90%).

M.p.: 247–250 °C (decomposition); IR (ATR) ν (cm^{-1}): 3067, 3048, 2957, 2916, 2853, 1730, 1724, 1719, 1576, 1558, 1545, 1485, 1429, 1331, 1308, 1287, 1273, 1263, 1254, 1153, 1142, 1123, 1072, 1065, 972, 947, 870, 818, 808, 795, 760, 737, 702, 671, 646, 517; ^1H NMR (300 MHz, CD_2Cl_2): δ = 8.08 (d, J = 2.1 Hz, 2H), 7.92 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.8 Hz, 2H), 7.32 (dd, J = 9.0, 2.1 Hz, 2H), 6.81 (d, J = 9.0, 2H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ = 137.6, 132.5, 131.7, 131.0, 130.6, 130.4, 128.3, 126.5, 124.2, 119.4, 15.7; HRMS (EI $^+$): m/z [M] $^+$ calcd for ($\text{C}_{22}\text{H}_{16}^{79}\text{Br}^{81}\text{BrS}_2$): 503.9040; found 503.9036.

Synthesis of 2^{Oct} : To a suspension of 2^{Br} (390 mg, 0.773 mmol) and $[\text{Pd}(\text{dppf})\text{Cl}_2]$ (29 mg, 0.039 mmol) in dry THF (25 mL) under N_2 , n -Oct-Mg-Br was added dropwise (3.8 mL of 1 M solution in THF) at 0 °C. The mixture was stirred at reflux for 2.5 h and then at rt overnight. NH_4Cl aq. sat. solution (20 mL) was added, and the mixture extracted with EtOAc (3 \times 20 mL). The combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography (petroleum ether/ CH_2Cl_2 5:1), to afford 2^{Oct} (310 mg, 70%) as a white glue.

IR (ATR) ν (cm^{-1}): 2955, 2920, 2853, 1578, 1493, 1458, 1433, 1377, 1335, 1312, 1260, 1140, 1119, 974, 880, 843, 802, 721, 679, 420; ^1H NMR (300 MHz, CDCl_3): δ = 7.91 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 1.7 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.09 (dd, J = 8.7, 1.7 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 2.72–2.62 (m, 4 H), 2.42 (s, 6H), 1.68–1.63 (m, 4H), 1.40–1.26 (m, 20H), 0.89–0.85 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ = 139.9, 135.3, 132.7, 131.7, 131.2, 128.7, 128.5, 126.6, 124.9, 123.4, 36.1, 32.0, 31.3, 29.6, 29.6, 29.4, 22.8, 16.0, 14.3; HRMS (APCI $^+$): m/z [M + H] $^+$ calcd for ($\text{C}_{38}\text{H}_{51}\text{S}_2$): 571.3432; found 571.3435.

Synthesis of 4^{H} and 4^{Oct} : To an oven dried flask containing compound 3^{H} (100 mg, 0.264 mmol) or 3^{Oct} (500 mg, 0.829 mmol) in 65 mL of dry CH_3CN , TfOH (1 mL) was added under N_2 , and the mixture stirred at 80 °C overnight. Pyridine (5 mL) was added to the reaction mixture and stirred overnight at 80 °C. After cooling to rt, pyridine was removed in vacuo, the residue dissolved in CH_2Cl_2 , washed with water and brine, dried with MgSO_4 , filtered and concentrated. The crude product was purified by column chromatography (neutral alumina Brockman activity 1, hexane/ CH_2Cl_2 20:1, gradient to pure CH_2Cl_2) to afford 4^{H} as an orange solid (37 mg, 45%) and 4^{Oct} as an orange solid (140 mg, 31%).

4^{H} : M.p.: 211–213 °C; IR (ATR) ν (cm^{-1}): 3042, 2920, 2851, 1593, 1543, 1508, 1499, 1474, 1458, 1414, 1358, 1315, 1281, 1206, 1163, 1155, 1115, 1074, 995, 966, 959, 874, 812, 777, 758, 744, 640, 630, 557, 550, 530; ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.27 (d, J = 8.7 Hz, 2H), 7.13 (dd, J = 8.1 Hz, 1.4 Hz, 2H), 7.01 (dd, J = 8.1, 7.3 Hz, 2H), 6.86 (dd, J = 7.3 Hz, 1.4 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ = 134.3 (C), 129.9 (C), 129.7 (C), 128.7 (CH), 126.2 (CH), 125.9 (C), 125.7 (C), 125.5 (CH), 125.2 (CH), 120.9 (CH); HRMS (APCI $^+$): m/z [M + H] $^+$ calcd for ($\text{C}_{20}\text{H}_{11}\text{S}_2$): 315.0302; found 315.0293.

4^{Oct} : M.p.: 120–122 °C; IR (ATR) ν (cm^{-1}): 3051, 2949, 2922, 2853, 1609, 1547, 1487, 1466, 1420, 1360, 1283, 1169, 1111, 1009, 941, 870, 839, 795, 773, 735, 554; ^1H NMR (300 MHz, CDCl_3): δ = 7.18 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 1.6 Hz, 2H), 6.74 (d, J = 8.7 Hz, 2H), 6.72 (d, J = 1.6 Hz, 2H), 2.50–2.45 (m, 4H), 1.58 (m, 4H), 1.31–1.26 (m, 20H), 0.88–0.86 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ = 141, 134.6, 129.6, 128.4, 128.3, 125.6, 125.6, 124.9, 124.1, 122.0, 35.5, 32.0, 30.9, 29.6, 29.4, 29.4, 22.8, 14.3; HRMS (EI $^+$): m/z [M] $^+$ calcd for ($\text{C}_{36}\text{H}_{42}\text{S}_2$): 538.2728; found 538.2715.

Synthesis of 7^{H} : To a suspension of 4^{H} (25 mg, 0.066 mmol) in CH_3COOH (5 mL), H_2O_2 (1 mL) was added, and the mixture refluxed overnight. After cooling down to rt a yellow precipitate which formed was washed with water and petroleum ether, and recrystallised from hot DMF. Recrystallisation did not allow purification, as an impurity also crystallised, and low solubility of the product did not allow purification with other methods. However, despite the crystallisation of impurity, it was possible to manually pick crystals of 7^{H} suitable for X-Ray diffraction.

Synthesis of 7^{Oct} : To a suspension of 4^{Oct} (30 mg, 0.056 mmol) in CHCl_3 (5 mL), $m\text{CPBA}$ (43 mg, 0.25 mmol) was added, and the mixture refluxed overnight. The mixture was cooled down to rt and concentrated under reduced pressure. The crude product was purified with silica gel chromatography (petroleum ether/ CH_2Cl_2 1:4, gradient to 2:5) to afford 7^{Oct} (27 mg, 90%) as a pale, yellowish solid.

M.p.: 184–186 °C; IR (ATR) ν (cm^{-1}): 2957, 2922, 2847, 1618, 1582, 1466, 1433, 1422, 1371, 1290, 1206, 1159, 1134, 1123, 1013, 974, 895, 822, 799, 775, 719, 662, 611, 588, 569, 557, 519; ^1H NMR (300 MHz, CD_2Cl_2): δ = 8.50 (d, J = 1.7 Hz, 2H), 8.45 (d, J = 8.7 Hz, 2H), 8.27 (d, J = 8.7 Hz, 2H), 8.11 (d, J = 1.7 Hz, 2H), 3.00–2.95 (m, 4H), 1.87–1.77 (m, 4H), 1.45–1.29 (m, 20H), 0.90–0.86 (m, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 145.0, 136.0, 135.3, 134.2, 134.0, 132.5, 128.7, 123.0, 121.9, 121.6, 36.2, 32.4, 31.3, 29.9, 29.8, 29.8, 23.2, 14.4; HRMS (APCI $^+$): m/z [M + H] $^+$ calcd for ($\text{C}_{36}\text{H}_{43}\text{O}_4\text{S}_2$): 603.2603; found 603.2603.

Synthesis of 8: To a stirred solution of 2,2'-dibromo-1,1'-binaphthalene (500 mg, 1.21 mmol) in dry THF (20 mL), TMEDA (0.40 mL, 2.7 mmol) was added under N_2 . n -BuLi (1.6 M solution in hexanes) (1.8 mL, 2.9 mmol) was added dropwise at -78 °C and the mixture stirred for 1 h. To the formed, greenish slurry (MeSe_2) (0.69 mL, 7.3 mmol) was added dropwise at -78 °C, and the reaction mixture was stirred overnight while slowly heating back to rt. Water (20 mL) was added and the mixture extracted with CH_2Cl_2 (3 \times 20 mL). The combined organic phases were dried with MgSO_4 , filtered and concentrated in vacuo. Purification by silica gel chromatography with petroleum ether/ CH_2Cl_2 (4:1) gave desired product **8** as a white solid (345 mg, 65% yield).

M.p.: 174–176 °C; IR (ATR) ν (cm^{-1}): 3049, 2980, 2928, 1614, 1578, 1555, 1499, 1420, 1395, 1373, 1339, 1317, 1273, 1254, 1165, 1150, 1134, 1125, 1107, 941, 910, 901, 843, 804, 779, 770, 743, 689, 546; ^1H NMR (300 MHz, CDCl_3): δ = 7.94 (d, J = 8.7 Hz, 2H), 7.90 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.7 Hz, 2H), 7.43 (ddd, J = 8.2, 6.8, 1.3 Hz, 2H), 7.25 (ddd, J = 8.5, 6.8, 1.3 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 2.28 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ = 135.6, 132.7, 132.3, 132.0, 129.0, 128.3, 127.1, 125.8, 125.5, 125.1, 6.6; HRMS (APCI $^+$): m/z [M + H] $^+$ calcd for ($\text{C}_{22}\text{H}_{19}^{78}\text{Se}_2$): 438.9833; found: 438.9840.

Synthesis of 10: To a two-neck oven-dried flask fitted with a condenser, compound **9** (50 mg, 0.11 mmol) was added under N_2 . TfOH (0.3 mL) was added, and the mixture stirred at 80 °C overnight. Pyridine (1.5 mL) was added, and the mixture stirred overnight at 100 °C. The cooled mixture was diluted with toluene, transferred to a round bottom flask and evaporated under reduced pressure. Water was added and the mixture extracted with toluene (1 \times 50 mL). The organic phase was washed with water (3 \times 20 mL) and brine (1 \times 20 mL), dried with MgSO_4 and concentrated in vacuo. Recrystallisation from hot toluene and hexane mixture afforded **10** as red needles (19 mg, 44%).

M.p.: 166–168 °C; IR (ATR) ν (cm^{-1}): 3046, 2980, 2889, 1717, 1595, 1541, 1506, 1456, 1418, 1395, 1387, 1339, 1258, 1204, 1157, 1105, 1070, 957, 806, 772, 746, 627, 546; ^1H NMR (300 MHz, CDCl_3): δ = 7.46 (d, J = 8.5 Hz, 2H), 7.36 (dd, J = 7.9, 1.4 Hz, 2H), 7.28 (dd, J = 7.3 Hz, 1.4 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 7.14 (dd, J = 7.9 Hz,

7.3 Hz, 2H); ^{13}C NMR could not be recorded due to poor solubility. HRMS (APCI⁺): m/z [M+H]⁺ calcd for (C₂₀H₁₁⁷⁸Se⁸⁰Se): 408.9199; found: 408.9187.

General procedure for chemical oxidation: To a solution of the relevant PTXTX derivative in 20–80 mL of 1:1 CHCl₃:CH₃COOH mixture, H₂O₂ (30–35% in water) was added and the mixture stirred for 4–6 h at rt. The reaction mixture was quenched with saturated NaOH aq. solution at 0 °C, until pH ~ 12. The mixture was extracted with CHCl₃. The combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo.

3^H: M.p.: 142–145 °C; IR (ATR) ν (cm⁻¹): 3055, 2997, 2913, 1584, 1503, 1412, 1403, 1308, 1256, 1161, 1032, 951, 872, 818, 787, 775, 748, 692, 677, 637, 496, 463; ^1H NMR (300 MHz, CD₂Cl₂) and ^{13}C NMR (75 MHz, CDCl₃) spectra of the diastereoisomeric mixture available in the Supporting Information; HRMS (ES⁺): m/z [M+H]⁺ calcd for (C₂₂H₁₉O₂S₂): 379.0826; found 379.0829.

3^{Oct}: IR (ATR) ν (cm⁻¹): 2853, 2361, 2342, 1578, 1491, 1458, 1433, 1375, 1337, 1312, 1258, 1119, 1057, 880, 814, 802, 669, 419; ^1H NMR (300 MHz, CDCl₃) and ^{13}C NMR (75 MHz, CDCl₃) spectra of the diastereoisomeric mixture available in the Supporting Information. HRMS (APCI⁺): m/z [M+H]⁺ calcd for (C₃₈H₅₁O₂S₂): 603.3330; found 603.3340.

5^H: M.p.: 240–242 °C; IR (ATR) ν (cm⁻¹): 3048, 2918, 2851, 1609, 1541, 1495, 1435, 1416, 1341, 1290, 1229, 1196, 1140, 1059, 1016, 959, 874, 854, 829, 816, 783, 752, 685, 673, 646, 604, 567, 530, 515, 496, 465, 453, 434, 409; ^1H NMR (300 MHz, CDCl₃): δ = 8.38 (dd, J = 7.2, 1.3 Hz, 1H), 8.14 (dd, J = 8.0, 1.3 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.7 Hz, 1H), 7.81 (dd, J = 8.0, 7.2 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.59 (dd, J = 7.6, 1.8 Hz, 1H), 7.48–7.43 (m, 2H), 7.41 (dd, J = 7.4, 1.8 Hz, 1H); ^{13}C NMR spectra could not be recorded due to low solubility of the product; HRMS (APCI⁺): m/z [M+H]⁺ calcd for (C₂₀H₁₁O₂S₂): 331.0251; found 331.0255.

5^{Oct}: M.p.: 142–144 °C; IR (ATR) ν (cm⁻¹): 3049, 2951, 2914, 2847, 1611, 1558, 1514, 1489, 1458, 1150, 1072, 1022, 982, 939, 880; ^1H NMR (500 MHz, CD₂Cl₂): δ = 8.21 (d, J = 1.7 Hz, 1H), 7.95 (d, J = 1.2 Hz, 1H), 7.92 (d, J = 8.7 Hz, 1H), 7.90 (d, J = 8.6 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.47 (d, J = 8.7 Hz, 1H), 7.41 (d, J = 1.2 Hz, 1H), 7.32 (d, J = 1.7 Hz, 1H), 2.95–2.91 (m, 2H), 2.75–2.72 (m, 2H), 1.80–1.77 (m, 2H), 1.72–1.70 (m, 2H), 1.41–1.27 (m, 20H), 0.89–0.87 (m, 6H); ^{13}C NMR (75 MHz, CDCl₃): δ = 142.8 (C), 141.6 (C), 137.6 (C), 134.9 (CH), 134.8 (C), 132.7 (CH), 132.6 (C), 131.7 (C), 131.1 (C), 130.8 (CH), 129.6 (CH), 128.8 (CH), 128.0 (C), 127.2 (C), 126.5 (C), 126.0 (CH), 124.1 (CH), 122.1 (CH), 121.4 (C), 119.6 (C), 35.8 (CH₂), 35.6 (CH₂), 32.0 (CH₂), 31.2 (CH₂), 31.1 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 22.8 (CH₂), 14.3 (CH₃) (6 carbon peaks are missing due to overlap); HRMS (APCI⁺): m/z [M+H]⁺ (C₃₆H₄₃O₂S₂): 555.2755; found 555.2758.

6^H: m.p.: 284–286 °C (decomposition); IR (ATR) ν (cm⁻¹): 3090, 3055, 3011, 2924, 2853, 1578, 1489, 1423, 1369, 1294, 1215, 1202, 1153, 1142, 1121, 1061, 1013, 835; ^1H NMR (300 MHz, CD₂Cl₂): δ = 8.43 (dd, J = 7.2, 1.2 Hz, 2H), 8.38 (dd, J = 7.2, 1.2 Hz, 2H), 8.30–8.27 (m, 8H), 8.23 (dd, J = 8.2, 1.2 Hz, 2H), 8.16 (dd, J = 8.2, 1.2 Hz, 2H), 7.92–7.84 (m, 4H); ^{13}C NMR (75 MHz, CDCl₃): δ = 137.7 (C), 136.8 (C), 136.5 (C), 135.8 (C), 135.2 (C), 134.6 (C), 133.4 (CH), 132.6 (CH), 132.3 (CH), 132.3 (CH), 131.5 (CH), 129.2 (CH), 128.1 (CH), 128.1 (CH), 126.5 (CH), 124.5 (CH), 122.4 (C), 122.1 (C) (2 carbon peaks are missing due to overlap); HRMS (APCI⁺): m/z [M+H]⁺ (C₂₀H₁₁O₂S₂): 347.0200; found 347.0211.

9: IR (ATR) ν (cm⁻¹): 3055, 2982, 1501, 1396, 1308, 1258, 1157, 1072, 899, 876, 799, 775, 748, 687, 671, 625; ^1H NMR (300 MHz, CDCl₃) spectra of the diastereoisomeric mixture available in the Supporting Information. ^{13}C spectra not recorded due to low solubility. HRMS

(APCI⁺): m/z [M+H]⁺ calcd for (C₂₂H₁₉O₂Se₂): 470.9731; found: 470.9745.

Crystallographic details: Deposition Number(s) 1869244 and 1869246 (for 4^H), 1869239 (for 4^{Oct}), 1869245 (for 5^H), 1869242 (for 5^{Oct}), 1869243 (for t-6^H), 1869240 (for 7^H), 1914850 (for anti-7^{Oct}), 1914851 (for syn-7^{Oct}), 2194810 (for 10), 1869241 (for 11^H), 2011130 (for (4^H)₃(ClO₄)₂), 2011129 (for (PXX)₂(ClO₄)₁) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Acknowledgements

D.B. gratefully acknowledges the EU through the MSCA-ITN-ETN (project: PHOTOTRAIN, No. 722591) and MSCA-RISE (project: INFUSION, No. 734834) programs and the University of Vienna for generous financial support. O.M. and T.B. thank the ITN-ETN PHOTOTRAIN project for their PhD fellowships. R.D.C. acknowledges the European Union's Horizon 2020 research and innovation FET-OPEN under the grant agreement ARTIBLED No 863170, the ERC-Co InOutBioLight No. 816856, and the MSCA-ITN StiBNite No. 956923. SM-V and EC thanks the support of the Spanish MCIN (2D-HETEROS Project PID2020-117152RB-100 and Excellence Unit "María de Maeztu" CEX2019-000919-M).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: mixed-valence complexes · organic semiconductors · polycyclic aromatic hydrocarbons · PXX · S-doping · thin-film lighting

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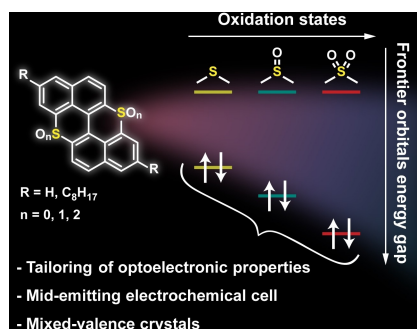
Manuscript received: October 6, 2022

Accepted manuscript online: November 4, 2022

Version of record online: ■■■, ■■■■

RESEARCH ARTICLE

Peri-thiaxanthenothioxanthene is used as a functional scaffold to engineer a molecular semiconductor, the properties of which can be tailored by editing the oxidation state of the S-atoms. Oxidation with H_2O_2 led to the relevant sulfoxide and sulfone congeners, whereas electrooxidation yields sulfonium-type derivatives forming crystalline mixed valence complexes.



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Tweaking the Optoelectronic Properties of S-Doped Polycyclic Aromatic Hydrocarbons by Chemical Oxidation

